

Rapid sun light degradation of Rhodamine-B, Methylene blue, Methyl orange, Congo red and their binary mixtures using suprastoichiometric Bi - Molybdate

P. Suresh, A.M. Umabala, A.V. Prasada Rao

Abstract— $\text{Bi}_2(\text{MoO}_4)_3$ with excess MoO_3 has been prepared by combustion method using Bismuth nitrate, MoO_3 and glycine. The sample as prepared showed excellent photocatalytic activity for the degradation of Rhodamine B, Methylene blue, Methyl orange and Congo red in presence of H_2O_2 under direct exposure to sun light. Complete degradation of separate 100ml aqueous solutions containing 5ppm Rhodamine B, 10ppm Methylene blue, 5ppm Methyl orange and 20ppm Congo red with 100 mg of dispersed catalyst occurred in 60, 120, 70 and 60 min respectively. Binary mixtures of aqueous solutions containing different dyes also showed complete bleaching in 60 to 150 min of exposure to sun light. Photoluminescence studies using terephthalic acid showed generation of $\cdot\text{OH}$ free radicals in the solution during irradiation. Synergistic effect is noticeable for $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ with MoO_3 towards degradation of pure dyes as well as their mixtures.

Index Terms— $\text{Bi}_2(\text{MoO}_4)_3$, Rhodamine B, Methylene blue, Methyl orange, Congo red, Photocatalytic degradation

I. INTRODUCTION

Rapid global industrialization over the past few decades led to significant contamination of our aquatic sources with pollutants capable of causing severe damage to living organisms. Especially since one to 20% of total world production of dyes is lost during dyeing process, the exhausts from leather and textile industries pose a serious ecological threat because the remnant dyes in the exhausts are less biodegradable, often carcinogenic and impart intense colors to effluents, thereby blocking the penetration of sun light and impairing the natural growth ability of aquatic life. Though common methods like ultra-filtration, reverse osmosis and adsorption are used for remediation of such hazardous waste water effluents, these techniques being non-destructive, simply cause transfer of pollutants from one phase to another leading to secondary pollution. Likewise, chlorination and ozonation have also been shown to be relatively less efficient and not cost effective. Recently, metal oxide semiconductor mediated heterogeneous photo catalysis has received considerable attention as an emerging destructive green technology for mitigation of hazardous aquatic organic pollutants. The main advantages of this process are (i) many

harmful organic effluents can be directly converted into CO_2 , H_2O and mineral salts without any toxic intermediates (ii) degradation can be effected at ambient temperature and (iii) photo degradation proceeds even at low concentrations (in the ppm level) of the organic pollutants. Anatase form of TiO_2 has been projected as suitable photo catalyst for this purpose because it is inexpensive, non-toxic and chemically inert. But the wide band gap of 3.2 eV limits the absorption of TiO_2 to U.V region below 390nm. To shift the absorption of TiO_2 into visible region so as to avail ~ 45% of solar radiation, different approaches have been reported in literature namely selective anion/cation/metal atom doping into TiO_2 lattice, photo sensitization with dyes/metal phthalocyanins/metal phorphyrins and formation of hetero structures with materials such as graphene etc. Alternately, a number of non- TiO_2 based mixed metal oxides such as ZnWO_4 , BiFeO_3 , Bi_2MoO_6 etc. have been explored as photo catalysts. Recently, the authors have reported the successful use of $\text{Fe}_2\text{Mo}_3\text{O}_{12} \cdot x\text{MoO}_3$ [1-3] and $\text{Bi}_2\text{Mo}_3\text{O}_{12} \cdot x\text{MoO}_3$ [4-5] as efficient photo catalysts for visible light degradation of organic dyes with different chromophores. In continuation of this work, the present paper describes rapid sun light induced photo degradation of Rhodamine B (Rh-B), Methylene blue (MB), Methyl orange (MO), Congo red (CR) and their binary mixtures over $\text{Bi}_2\text{Mo}_3\text{O}_{12} \cdot x\text{MoO}_3$ in presence of an external oxidant H_2O_2 .

II. MATERIALS AND METHODS

A. Synthesis and characterization of photo catalyst

$\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ and MoO_3 of AR Quality were starting materials, 5.40307g $\text{Bi}(\text{NO}_3)_3$ and 4.80992g MoO_3 ($\text{Bi} : \text{Mo} = 1:3$) were added to 50 ml of water under constant stirring followed by the addition of 0.50171g of glycine. The precursor solution containing dispersed MoO_3 was then heated on a hot plate at 110°C until it became viscous with liberation of large amounts of brown fumes. The dried mass was then calcined at 400°C for 4 hrs. The resultant powder was ground and used for phase identification by X-ray diffraction (XRD).

B. Photo catalytic studies

Photo catalytic activity of $\text{Bi}_2(\text{MoO}_4)_3$ was evaluated in terms of degradation of Rhodamine B, Methylene blue, Methyl orange and Congo red under sun light. 100 mg of the catalyst powder was added into 100ml Rh-B aqueous solution (5 mg/L). Before irradiation the suspension was magnetically

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stirred for 30 minutes in dark. The suspension was then exposed to sun light; 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. Progress of decolorization was followed by recording the corresponding absorption spectrum. The same procedure has been adopted for (10mg/L) MB, (5mg/L) MO and (20mg/L) CR dyes. All the experiments were conducted under ambient conditions. Extent of degradation of dye is calculated by using the expression.

$$\% \text{ degradation} = (A_0 - A_t / A_0) 100$$

where A_0 and A_t are respectively initial absorbance and absorbance at time 't'

C. Photoluminescence studies

50mg $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ catalyst is added to 100ml of terphthalic acid (TPA) solution (0.25 mmol L^{-1} in 1mmol L^{-1} NaOH solution). The solution is stirred for 30min in dark followed by irradiation by 400w metal halide lamp for 45min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectrometer (Fluoromax 4) with the excitation wavelength of 315nm.

III. RESULTS AND DISCUSSION

Fig. 1 depicts XRD pattern of the mixture of Bi-nitrate, MoO_3 and glycine mixed in water, dried and calcined at 400°C for 4 hrs. All the observed peaks could be indexed to $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and MoO_3 of JCPDS files 70-1396 and 76-1003 respectively. Absence of peaks due to Bi_2O_3 and other phases of Bi and Mo - oxides indicates complete formation of $\text{Bi}_2(\text{MoO}_4)_3$ coexisting with excess MoO_3 .

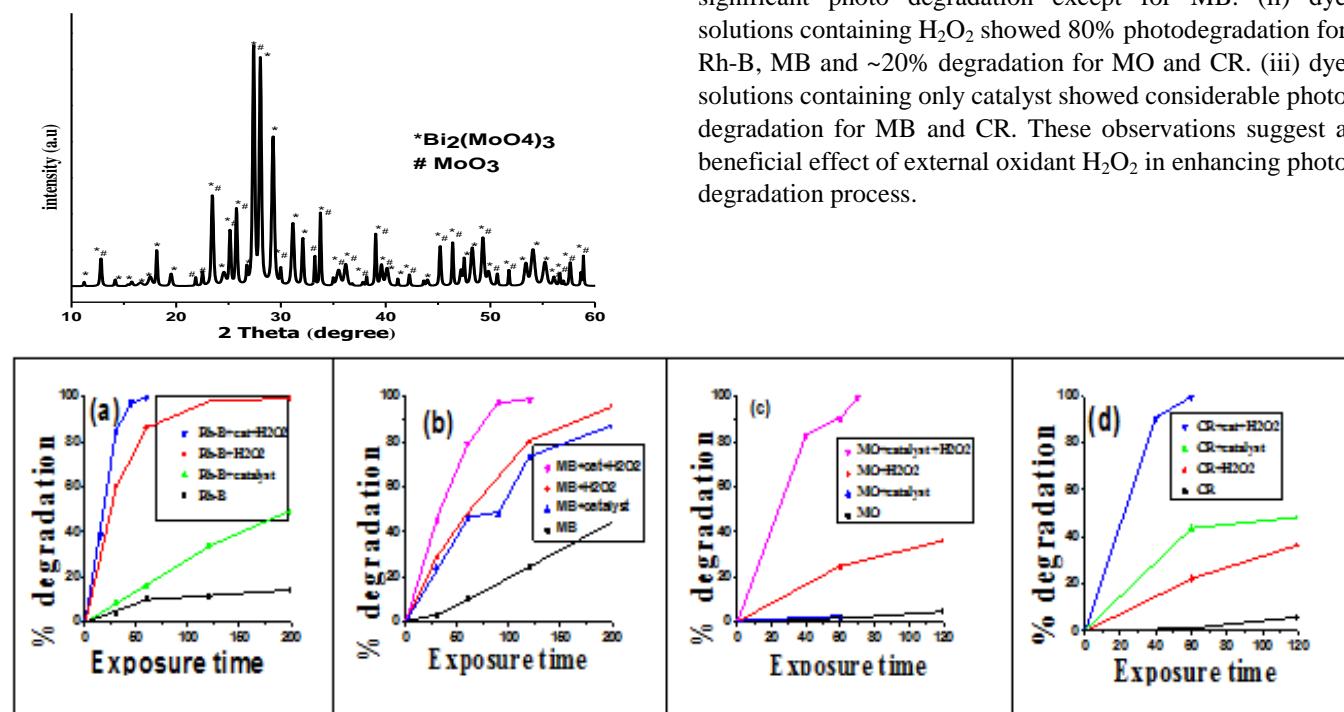


Fig 2. Variation of % degradation of pure dye solution, dye solution + H_2O_2 , dye solution + catalyst and, dye solution + catalyst+ H_2O_2 as a function of exposure time for aqueous solutions of (a) Rh-B, (b) MB, (c) MO and (d) CR

Photodegradation is further aided by excess MoO_3 present in supra stoichiometric $\text{Bi}_2\text{Mo}_3\text{O}_{12}.\text{xMoO}_3$. Since MoO_3 is an n-type semiconductor with a band gap equal to 2.9 eV which

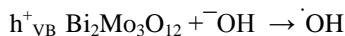
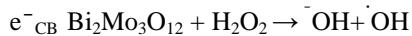
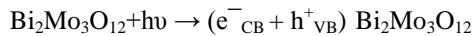
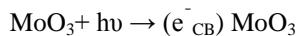
Fig 1. XRD pattern of resulting powder obtained from Bismuth nitrate, Molybdenum oxide and Glycine in water, heat treated at 400°C for 4 hr.

Photo degradation of Rh-B was reported over $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$ [6], TiO_2/ZnO [7], TiO_2 and ZnO [8], ZnO [9-10], and Pt-TiO_2 [11], In all these cases, the reported photo degradation times varied from 130 to 360min. Photo degradation of MB was reported over Ag/TiO_2 [12], Nano TiO_2 [13-14], nano ZnO [15], TiO_2 [16], W/Mo doped TiO_2 [17], Graphene oxide/ TiO_2 [18]. Reported degradation times varied from 60 to 300min. Degradation of MO was reported over nano SnO_2 [19], TiO_2 [20], CuO doped ZnO [21], Ag/N-TiO_2 [22], Cr-doped ZnS [23], ZnO/Zn-stannate [24], nano ZnO [25], $\alpha\text{-Fe}_2\text{O}_3$ [26], Er^{3+} : $\text{YAlO}_3/\text{TiO}_2$ [27]. In the above reports, except for Er^{3+} : $\text{YAlO}_3/\text{TiO}_2$ and Ag/N-TiO_2 the irradiation source is U.V and photo degradation times varied from 80 to 540min, and even for those with visible light irradiation, photo degradation times were rather high (480min). Photo degradation of CR has been studied with TiO_2 [28-31], SnO_2 [32], ZnO [33], ZrO_2 [34], $\text{TiO}_2/\text{Fe}_3\text{O}_4$ [35], and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ [3] photo catalysts under U.V irradiation except for $\text{Fe}_2\text{Mo}_3\text{O}_{12}$.

Variation of percent degradation of pure dye solution, dye solution+ H_2O_2 , dye solution+catalyst and dye solution + H_2O_2 +catalyst as a function of exposure time for Rh-B, MB, MO and CR are depicted in Fig 2. From the figure, it can be seen that complete degradation for Rh-B, MB, MO and CR dye solutions in presence of H_2O_2 and catalyst occurred in 60, 120, 70 and 60 minutes respectively. For the above degradation times (i) pure dye solutions did not show any significant photo degradation except for MB. (ii) dye solutions containing H_2O_2 showed 80% photodegradation for Rh-B, MB and ~20% degradation for MO and CR. (iii) dye solutions containing only catalyst showed considerable photo degradation for MB and CR. These observations suggest a beneficial effect of external oxidant H_2O_2 in enhancing photo degradation process.

is less than the band gap of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (3.1 eV), absorption of electromagnetic radiation by MoO_3 causes excitation of e^- which will be subsequently transmitted to conduction band of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Also, on absorption of electromagnetic radiation

$\text{Bi}_2\text{Mo}_3\text{O}_{12}$ generates e^- and hole in its conduction band and valence band respectively. Availability of e^- in the conduction band of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ is thus enhanced due to synergistic effect of MoO_3 and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Based on the above discussion, the following mechanism is proposed for the photo degradation of dyes under investigation.



Dye + $\cdot\text{OH} \rightarrow$ Dye degradation products

In order to ascertain the formation of $\cdot\text{OH}$ radicals consequent to irradiation, terephthalic acid (TPA) is used as probe molecule. TPA is known to react with $\cdot\text{OH}$ radicals to produce 2-hydroxy terephthalic acid (TAOH) which is highly fluorescent with wave length intensity around 419nm. Photoluminescence spectra for the solution of TPA mixed with photocatalyst + H_2O_2 prior to irradiation and after irradiation are shown in Fig 3. High intense peak at 419nm after irradiation is a clear indication of the formation of $\cdot\text{OH}$ radicals. This is further confirmed in terms of increase in degradation times for Rh-B in presence of scavengers HCO_3^- and manitol shown in Fig. 4.

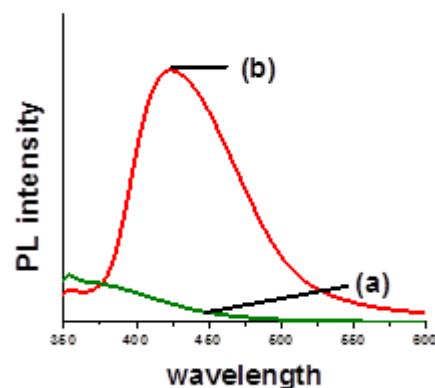


Fig. 3. Photoluminescence spectrum of TPA mixed with aqueous solution of H_2O_2 containing $\text{Bi}_2(\text{MoO}_4)_3$ (a) prior to irradiation and (b) after irradiation

Rate constants derived from the plots of $\ln C/\text{Co}$ vs time for dye solution, dye solution + H_2O_2 , dye solution + catalyst and dye solution + H_2O_2 + photo catalyst for Rh-B, MB, MO and CR are given in Table 1. Relative magnitudes of the observed rate constants also suggest a beneficial effect due to H_2O_2 in the photo degradation process.

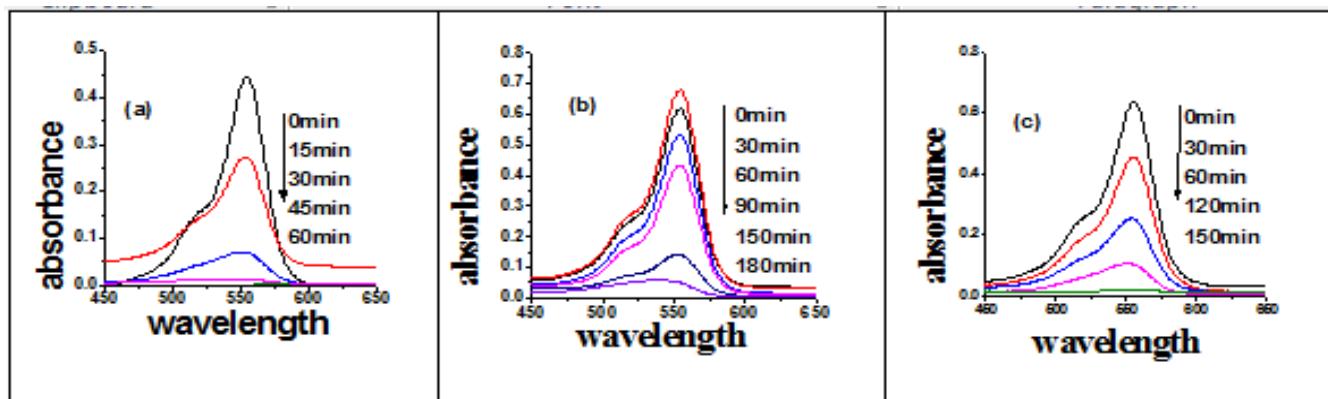


Fig. 4. Temporal evolution of spectral changes of Rh-B aqueous solution as a function of irradiation time in presence of (a) photocatalyst + H_2O_2 , (b) photocatalyst + $\text{H}_2\text{O}_2 + \text{HCO}_3^-$, and (c) photocatalyst + $\text{H}_2\text{O}_2 + \text{manitol}$

Table 1. Rate constants derived from $\ln C/\text{Co}$ vs exposure time plots for Rh-B, MB, MO and CR dyes under different conditions.

Components in solutions exposed to irradiation	Rate constants for photo degradation of			
	Rhodamine B	Methylene blue	Methyl orange	Congo red
Dye only	4.5×10^{-6}	1.3×10^{-5}	3.3×10^{-6}	3.3×10^{-6}
Dye + H_2O_2	1.3×10^{-4}	7.5×10^{-5}	3.3×10^{-5}	3.3×10^{-5}
Dye + Catalyst	6.0×10^{-5}	2.1×10^{-4}	3.3×10^{-5}	1.2×10^{-4}
Dye + Catalyst+ H_2O_2	1.6×10^{-3}	2.9×10^{-4}	6.2×10^{-4}	2.7×10^{-4}

Photo catalytic efficiency of the catalyst is further explored for decolorisation of some binary mixtures of the above dyes. Four binary mixtures of dye aqueous solutions containing

5ppm MB+5ppm MO, 20ppm CR+5Ppm Rh-B, 5ppm MO+5ppm Rh-B and 5ppm MB+ 20 ppm CR each mixed with H_2O_2 and 100mg catalyst are exposed separately to direct sun light. Time dependent variations of absorption spectra of these mixed solutions as a function of exposure time to direct sun light are shown in Fig 5.

From the figure, it can be seen that complete disappearance of absorption intensity of above mixtures occurred in 60, 60, 90 and 150min respectively. Decrease in spectral intensities at respective λ_{max} values of constituent dye solutions in each case is accompanied with a simultaneous increase in intensity of the peak around 300nm indicating that degradation of dyes occur through the formation of an intermediate having absorption in the U.V region. The present method offers some specific advantages namely -use of bulk catalyst synthesized at low temperature, effective exploitation of naturally available solar radiation, non- requirement of pH adjustment

prior to irradiation, and cost effective ness based on green technology.

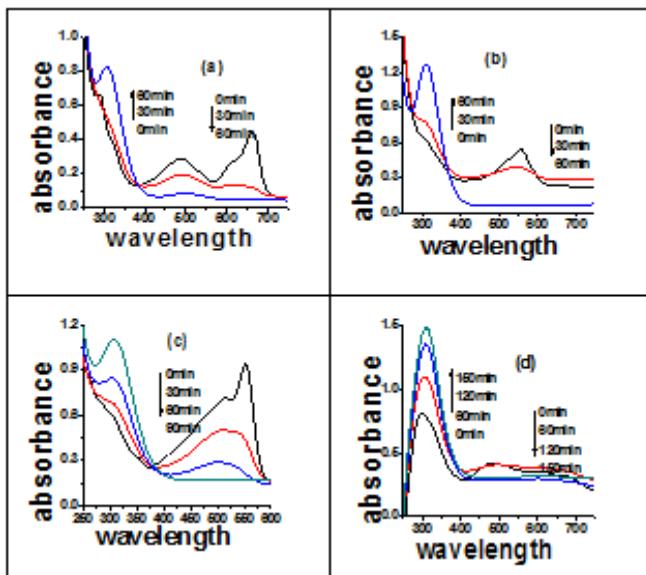


Fig. 5. Time dependent variation of absorption spectra relating to binary mixtures of 5ppm MB+5ppm MO, (b) 20ppm CR+5ppm Rh-B, (c) 5ppm MO+5ppm Rh-B and (d) 5ppm MB+20ppm CR as a function of exposure time to sun light.

IV. CONCLUSIONS

$\text{Bi}_2\text{Mo}_3\text{O}_{12}$ with excess MoO_3 prepared by combustion method showed good photo catalytic activity for the degradation of Rh-B, MB, MO and CR in presence of H_2O_2 . Separate 100 ml aqueous dye solutions containing 5 ppm Rhodamine B, 10ppm Methylene blue, 5ppm Methyl orange and 20ppm Congo red showed complete decoloration in 60, 120, 70 and 60 min respectively under direct sun light exposure. Mixed dye solutions containing 5ppm MB+5ppm MO, 20ppm CR+5Ppm Rh-B, 5ppm MO+5ppm Rh-B and 5ppm MB+ 20 ppm CR also got decolourised under to sun light in 60, 60, 90 and 150 minutes respectively. Photo catalytic degradation is ascribed to synergistic effect due to $\text{Bi}_2\text{Mo}_3\text{O}_{12} \cdot x\text{MoO}_3$ and H_2O_2 causing more 'OH free radicals to be generated as evidenced by photo luminescence studies using of terphthalic acid. Enhancement of 'OH free radicals led to rapid degradation of dyes as well as their binary mixtures.

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